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VELOCITY AND ABSORPTION OF ULTRASOUND IN BERYLLIUM OXIDE CERAMIC

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The ultrasound wave propagation velocity and absorption of ultrasound in samples of beryllium ceramics of varying density, shape, and size that differed by the molding method and degree of texturing of BeO microcrystals were investigated at room and low temperatures (approximately 100 K). It was found that the ultrasound propagation velocity increases with an increase in the density of the samples. It was shown that the ultrasound velocity in beryllium ceramics without specially added dopants is weakly dependent on the frequency in the 5 – 25 MHz range.

Measuring the velocity and absorption of ultrasound in ceramic materials is revealing ways of creating technical devices for transmission of ultrasound energy with minimum losses in a wide temperature range.

Of the oxide ceramic materials, a high-temperature, chemically, thermally, and radiationally resistant beryllium oxide ceramic is drawing great attention. The area of its application in different technical sectors is expanding. Articles made of beryllium ceramic are widely used in special metallurgy (for example, in melts of different metals and salts which have high temperatures, up to 2170 K), atomic, laser, electronics, electrical, and other sectors of industry, and special instrument making (RF patents Nos. 2141120, 2258331, 2248336) [1 – 7].

Propagation of ultrasound waves in different ceramic materials has been insufficiently investigated. Measurements in different types of oxide ceramics (BeO, Al_2O_3, ZrO_2, MgO, etc.) showed that a dense BeO ceramic has the highest ultrasound velocity. For this reason, studying the features of propagation and absorption of ultrasound in beryllium ceramics at high (up to 2170 K), room, and low temperatures is pressing.

The samples for the studies were obtained with ordinary ceramics technology — by semidry compression molding, slip casting (slips on organic base), and extrusion of plastic ceramic mass on organic base. Both the pure ceramic (with no specially added dopants) and ceramic based on BeO with TiO_2 dopants were used for the experiments. Ceramic articles in the form of rods, wafers, disks, and rings of different thickness and density were fabricated.

The BeO powder used for fabrication of the ceramic articles was represented by microcrystals of different morphology — primarily in the form of a mixture of idiomorphic hexagonal-prismatic crystals and in a smaller volume, rhombic and tetrahedral habit (see Fig. 1).

Using the petrographic method, it was found that in molding articles by semidry compression molding and slip casting, predominant stacking of the microcrystals perpendicular to the applied force (in compression molding) and perpendicular to the gravitational force in slip casting (texturing) is observed. Since most of the BeO microcrystals are spread along polar axis *c* and differ in properties as a function of the crystallographic direction, anisotropy of their physicochemical properties is established in molding of ceramic articles. The ceramic obtained by extrusion of the ceramic paste differed because the microcrystals were lined up so that their polar axes were primarily positioned parallel to the direction of extrusion. For this reason, the degree of texturing in the given case increased in comparison to other ceramic molding methods. Due to the absence of large BeO single crystals, we were unable to determine the difference in the ultrasound wave propagation velocity in BeO as a function of the crystallographic direction.

Use of different methods of molding the beryllium ceramic allowed qualitatively studying the effect of the method of fabricating the samples on the velocity and absorption of ultrasound in them.

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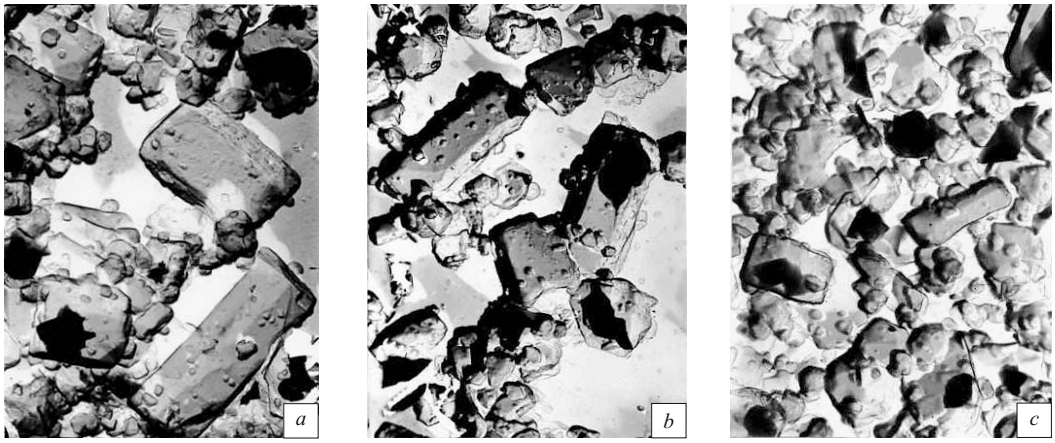

Fig. 1. Photomicrographs of beryllium oxide powders for slip preparation and molding: *a*, *b*) idiomorphic hexagonal-prismatic crystals (× 8000); *c*) hexagonal crystals and segregation formations of spherical crystals (× 12,000).

The measurements were performed at frequencies of 5, 10, 20, and 25 MHz on a specially built Intratest-1 unit,[2] Peleng UDZ-103 defectoscope (version 390), and P111-25 transformer. Machine oil was used in the measurements for eliminating the gap and transmitting the ultrasound from the piezoelectric emitter to the sample.

The methods of measuring ultrasound velocity can be divided into resonance, interferometer, pulsed, and optical [7 – 9]. The highest accuracy of measurement is attained in using pulsed-phase methods. We used the pulsed method for measuring ultrasound velocity and absorption in the different samples of the beryllium ceramic.

In addition to longitudinal and transverse waves, there are also other types of waves in samples of limited dimensions. Normal waves are propagated in wafers, rods, and hollow cylinders, and their velocity is not only determined by the elastic characteristics of the substance but also to some degree by the geometric dimensions of the articles and the predominant orientation of the microcrystals in them.

For this reason, we measured the ultrasound wave propagation velocity in the samples of BeO ceramic of different sizes and shapes and also with different apparent density and degree of texturing. A large number of measurements of ultrasound velocity and absorption in the ceramic samples was performed at a frequency of 5 MHz. The velocity and absorption coefficient of the ultrasound wave at 5 MHz and 300 K in the different samples of beryllium ceramic and SiO_2 single crystal are reported in Table 1.

The studies of the ultrasound velocity in a BeO ceramic rod made by extrusion of a plastic ceramic mass on an or-

[2] The measurements were performed by R. R. Danislamov (Intratest, Ekaterinburg) and A. S. Kurkov (Altek NPG, St. Petersburg).

TABLE 1

Sample No.	Sample type, molding method	Density, g/cm^3	Dimensions, mm			Direction of measurement	Sound velocity, km/sec	Sound absorption, dB/mm
			length	width	height			
1	Bar, extrusion	2.97	99.00	6.00	6.00	Along length	10.4 ± 0.3	0.05
						Across length	12.1 ± 0.4	0.20
2	Disk 60 mm in diameter, slip casting	2.98	–	–	4.50	From end	12.5 ± 0.4	–
3	Wafer, semidry compression molding	2.95	54.90	40.00	5.00	Along length	11.7 ± 0.3	–
4	Bar, slip casting	2.89	43.10	7.70	7.70	Same	11.3 ± 0.3	–
5	Rectangular parallelepiped, slip casting	2.97	60.00	34.00	7.70	″	11.9 ± 0.3	Average value 0.20
						Along width	11.5 ± 0.3	
						Along height	12.5 ± 0.3	
6	Wafer, slip casting	2.97	42.80	34.00	7.70	Along length	11.3 ± 0.3	–
7	Disk 85.0 mm in diameter, semidry compression molding	2.57	–	–	17.12	From ends	10.3 ± 0.3	0.15
8	SiO_2 single crystal	–	17.60	14.75	14.55		5.9 – 6.3	–

ganic base (sample No. 1) showed that the ultrasound velocity along the length of the article was 10.4 ± 0.3 km/sec, while it increased significantly in the transverse direction (12.1 ± 0.4 km/sec). The damping factor in this sample was equal to 0.05 dB/mm in the longitudinal direction and increased significantly in the transverse direction (0.15 dB/mm).

The ultrasound wave velocity in sample No. 2, fabricated by slip casting (BeO disk with density of 2.98 g/cm^3 and 4.5 mm thick) was 12.5 ± 0.4 km/sec at different points from its end. The ultrasound velocity in a flat part 54.9 mm long with a density of 2.95 g/cm^3, made by semidry compression molding (sample No. 3), was at the level of 11.7 ± 0.3 km/sec.

In the ceramic sample in the shape of a rod (sample No. 4) with a 43.1 m length of the side and density of 2.89 g/cm^3 fabricated by slip casting, the sound velocity was 11.3 ± 0.3 km/sec in the longitudinal direction, and in a similar sample 7.7 mm thick with a density of 2.97 g/cm^3, the average sound velocity was equal to 11.6 ± 0.4 km/sec. Repeated measurements of the ultrasound wave velocity conducted in a sample of the ceramic with a density of 2.97 g/cm^3 in the shape of a rectangular parallelepiped fabricated by slip casting (sample No. 5) along the length, width, and thickness, respectively 60, 34, and 7.7 mm, showed the following values of the velocity: 11.9 ± 0.3, 11.5 ± 0.3, and 12.5 ± 0.4 km/sec. As a result of many measurements of the ultrasound wave absorption factor in a given sample, the average value was established: 0.20 dB/mm.

The ultrasound velocity in the longitudinal direction in a rectangular BeO wafer 42.8 mm long with density of 2.97 g/cm^3 was 11.3 ± 0.3 km/sec (sample No. 6).

The change in the velocity and absorption of the ultrasound wave in a BeO disk 85 mm in diameter, 17.12 mm thick, with a comparatively low density of 2.57 g/cm^3 is especially interesting. This disk was fabricated by semidry compression molding and subsequent sintering at 2220 K in a forevacuum. The ultrasound studies at different points from the end of the disk showed that the average velocity of the ultrasound wave was equal to 10.3 ± 0.3 km/sec, and the average value of the ultrasound absorption coefficient was 0.15 dB/mm.

To check the accuracy of operation of the unit for measuring the ultrasound propagation velocity, experiments were conducted on a monocrystalline sample of SiO_2 (sample No. 8) The single crystal was grown by the hydrothermal method in an autoclave. A rectangular sample measuring 17.6 × 14.75 × 14.55 mm was arbitrarily cut from it. All facets of the parallelepiped were carefully polished, and the measurements were then performed. It was found that the ultrasound velocity in the sample varied within the range of 5.92 – 6.30 km/sec as a function of the direction of the facets. According to handbook data [7], the ultrasound velocity in SiO_2 along axes x and z is 5.600 and 6.330 km/sec, which satisfactorily correlates with the results of our measurements (see Table 1).

TABLE 2

Length of ceramic sample, mm	Sound velocity, km/sec	Sound absorption, dB/mm
29.50	11.50	0.15
50.00	10.80	0.15
70.60	11.15	0.15
89.40	10.76	0.02
120.95	10.55	0.02

A change is thus observed in the sound wave propagation velocity caused by anisotropy of the physicochemical properties in the beryllium ceramic. It was found that the ultrasound wave damping factors in BeO articles varied within the range of 0.05 – 0.20 dB/mm.

The results of measuring ultrasound velocity and absorption at the frequency of 5 MHz in ceramic rods of the same diameter (9.0 mm) fabricated with the same technology (extrusion of the plastic ceramic mass on an organic base at 300 K) and differing only in the length are reported in Table 2. A waveguide effect was found, caused by the fact that the diameter of the piezoelectric ultrasound emitter was much larger than the diameter of the samples measured (9.0 mm).

The sound velocity in the same samples — rods 50.00 and 89.40 mm long (Peleng UDZ-103 instrument) — was 11.0 and 11.4 km/sec, respectively. Slightly different values of the ultrasound wave propagation velocity were obtained with instruments from Spectrum-Group Association[3] at a frequency of 40 kHz. The measurements of the ultrasound velocity performed on the same samples 50.00 mm and 120.95 mm long showed the following values; 10.417 and 11.005 ± 0.02 km/sec, respectively.

The studies showed that the average ultrasound wave velocity in the samples of the beryllium ceramic varied from 10.3 to 12.5 km/sec. Such fluctuations are due to the different density of the sintered articles (it varied from 2.57 to 2.98 g/cm^3), the average microcrystal size, and the degree of texturing (specific stacking) of the microcrystals in the sintered articles.

The velocity and absorption of ultrasound were investigated in macrocrystalline ceramic samples made from BeO powder fired at high temperatures (approximately 2000 K) by slip casting. Before the measurements, the cylinders were carefully polished on the inside, outside, and from the ends. The ultrasound velocity and absorption were measured repeatedly.

The samples were hollow cylinders with an outer diameter of 40 mm and a height of 100 mm. The wall thickness was 4 mm. The density of the sintered samples was equal to 2.98 g/cm^3. The measurements were performed by the pulsed method along the walls of the cylinder at a frequency

[3] The measurements were performed under the direction of Dr. V. G. Shevaldykin (Spectrum-Groups Association, Moscow).

TABLE 3

Sample and measurement No.	Ground signal, μsec		Sound velocity, km/sec	Ground signal amplitude, dB		Absorption, dB/mm
	first $2\tau_1$	second $2\tau_2$		first	second	
1.1	18.55	36.25	11.20	15.8	22.3	0.032
1.2	18.55	36.35	11.23	20.4	28.6	0.041
1.3	18.55	36.45	11.17	19.6	26.4	0.034
1.1*	18.55	36.45	11.17	18.7	29.3	0.053
2.1	18.55	36.29	11.27	14.2	24.1	0.049
2.2	18.71	36.45	11.27	13.3	22.4	0.045
2.3	18.71	36.61	11.17	14.1	23.1	0.045

* In the given case, the measurements were performed from the opposite side of the ceramic cylinder, opposite point No. 1.1.

TABLE 4

Frequency of measurement, MHz	Direction of measurements in sample, mm		Sound velocity, km/sec	Total signal amplification in sample in cooling from 300 to approximately 100 K, dB
	along	across		
5	99	–	10.03	4.50
5	60	–	10.32	5.10
10	–	10	11.20	5.01

of 5 MHz. The ultrasound velocity and absorption at 5 MHz at different points of the BeO ceramic cylinders (Nos. 1 and 2) are reported in Table 3.

The average values of the ultrasound wave velocity at different points on two ceramic cylinders were close and were 11.19 – 11.23 km/sec, while the absorption was in the range of 0.040 – 0.046 dB/mm.

The petrographic studies of the average grain size in the samples showed that they had a macrocrystalline structure — the average size of the microcrystals was 65 – 70 μm. The ceramic samples had a high ultrasound wave propagation velocity probably for this reason. Absorption of ultrasound in this ceramic was also low. Measurements of the ultrasound velocity at other frequencies (10, 15, and 25 MHz) showed close values. On this basis, we can hypothesize that the velocity of ultrasound in the beryllium ceramic without specially added dopants is weakly dependent on the frequency in the 5 – 25 MHz frequency range.

The ultrasound velocity and absorption in beryllium ceramic wafers 2.9 mm thick with 30 wt.% TiO_2 were measured. The wafers were made by semidry compression molding and subsequent sintering in a forevacuum and in a reducing atmosphere. The dense ceramic wafers had an apparent density of 3.2 g/cm^3 and comparatively high electric conductivity. The measurements were made with a UDZ-103 instrument at frequencies of 15 and 25 MHz. It was found that the ultrasound velocity in the wafers was 10.74 and 10.40 km/sec. The damping measurements at different points of the BeO + TiO_2 ceramic wafers showed a significant increase in the damping factor in the 0.46 – 0.79 dB/mm range in comparison to pure (with no special additives) samples. The TiO_2 dopant phase in the amount of 30% thus also affects the propagation velocity of the ultrasound wave (slightly decreasing it), but most importantly, it significantly increases the ultrasound absorption coefficient.

The experiments on measuring the ultrasound velocity and absorption in the conditions of cooling the ceramic samples were of special interest, since such measurements have not been conducted previously.

Changing the frequency did not significantly change the velocity and absorption of the ultrasound wave. Going from 5 MHz to 15 – 25 MHz increased the accuracy of determining the ultrasound wave velocity in samples of the ceramic with small linear dimensions.

The measurements were performed as follows. The ultrasound emitter was glued to the ceramic sample, in the shape of small rods of varying length (the width and thickness were 10 mm) with Loctite glue. The ultrasound propagation velocity and value of the amplitude of the ultrasound wave in the sample was determined at room temperature. The samples were then immersed in a beaker with liquid nitrogen for 60 – 120 sec and the ultrasound velocity and amplitude were measured again. The temperature of the samples was not measured. The qualitative picture of the change in the relative parameters of the ultrasound wave in the ceramic samples as they cooled was observed. The change in the relative value of the ultrasound signal for the different samples of the beryllium ceramic as a function of the temperature are reported in Table 4.

Cooling the samples did not significantly alter the ultrasound wave velocity. Only an important increase in the amplitude of the propagated ultrasound wave was observed during cooling, probably due to an increase in the average path length of the phonons in the ceramic and a decrease in absorption of ultrasound energy.

For dielectrics with a large forbidden band width such as BeO (E_g ~ 10.8 eV), the energy losses on passage of ultrasound are due to phonon-phonon scattering. At a temperature significantly lower than the Debye temperature Θ_D (for BeO Θ_D ~ 1200 K), flip-over of the wave vector on collision of phonons can be neglected. In this case, the free path of the phonons $l \sim \exp \Theta_D / 2T$, i.e., the value of l increases with a decrease in the temperature. This process continues until l reaches the average size of the microcrystal. This also explains the decrease in the ultrasound energy losses with a decrease in the temperature. In the case of higher temperatures (above Θ_D), $l \sim 1/T$, i.e., l decreases and the ultrasound energy losses increase correspondingly with an increase in the temperature.

The experiments showed that this is also characteristic of other types of oxide ceramics, for example, Al_2O_3 and Y_2O_3 ceramics. On the other hand, heating the ceramic samples

TABLE 5

Index	Calculated values	Experimental data
Average sound velocity, km/sec	7.656	8.240 [10]
Debye temperature, K	1188	1280 [10, 11]
Maximum sound velocity (data from our measurements), km/sec	–	Up to 12,500
Compression modulus, GPa	198.39	210 [11]
Shear modulus, GPa	145.59	142 [12]
		102 [13]

from approximately 100 to 300 K increased absorption of ultrasound.

There are no experimental data on the change in the ultrasound velocity when ceramics samples are heated to high temperatures. We could predict that an increase in the temperature will make the ceramic less rigid and consequently reduce the ultrasound velocity and modulus of elasticity, thus increasing absorption of ultrasound energy by decreasing the indexes of the elastic properties of the BeO microcrystals. The experimental difficulties in measuring the velocity and absorption of ultrasound in beryllium ceramics at high temperatures (above 470 K) did not allow us to do this.

Beryllium oxide crystallizes in a hexagonal system and has structural type B4 (wurtzite, space group C6mc). The sound velocity in solids is determined by the moduli of elasticity of the substance. We estimated a series of thermomechanical parameters of pure BeO ceramic (shear modulus, compression modulus, average sound velocity) in comparison to the experimental data obtained by others (Table 5) based on the results of first-principle quantum-chemical calculations of the elastic constants of BeO single crystal and their subsequent approximation for beryllium ceramics.

The sound propagation velocity ν can be expressed in terms of the elastic parameters of the crystal. The average sound velocity $\overline{v}$ is calculated as:

$$\overline{v} = \left[\frac{1}{3} \left(\frac{2}{v_s^3} + \frac{1}{v_l^3} \right) \right]^{-\frac{1}{3}},$$

where v_s and v_l are respectively the transverse and longitudinal components of the sound velocity.

In the calculation with the above equation, we obtained $\overline{v} = 7.656$ km/sec. The experimental value is $\overline{v} =$ 8.240 km/sec [10].

The data from our measurements of the ultrasound velocity in samples of BeO of different shape and size (see Tables 1 – 4) differed significantly from the calculated and experimental values of other investigators [10, 11] (see Table 5).

It was thus experimentally shown that the ultrasound velocity in the beryllium ceramic is a function of:

the type of oxide; the BeO ceramic had a high ultrasound wave propagation velocity (up to approximately 12.5 km/sec); much lower ultrasound velocities were characteristic of single crystals of SiO_2;

the density of the samples obtained; the ultrasound propagation velocity increased with an increase in the density of the samples;

the predominant orientation of the BeO microcrystals in the samples, since some differences were observed in the ultrasound wave propagation velocity in samples made by semidry compression molding, slip casting, and to the greatest degree, in extrusion of the ceramic mass in measurement along and across the direction of drawing.

Cooling the ceramic samples from 300 to 100 K was not associated with important changes in the ultrasound propagation velocity in the samples. There was a significant increase in the amplitude of the ultrasound wave, due to a decrease in absorption of ultrasound in the samples caused by an increase in the average free path of phonons. Heating the ceramic samples, on the contrary, increased absorption of ultrasound in them.

The ultrasound velocity in beryllium ceramics without specially added impurities was weakly dependent on the frequency in the 5 – 25 MHz range. TiO_2 impurity phase in the amount of 30% also affected the ultrasound wave propagation velocity (by slightly decreasing it), but more important, the ultrasound absorption coefficient increased significantly.

The ultrasound velocity in BeO is minimum when observed along the polar axis of the BeO crystal, and the absorption coefficient has the minimum value and vice versa.

The basic characteristics established for the beryllium ceramic are also characteristic of other types of oxide ceramics (ZrO_2, Al_2O_3, and others).

Based on these experiments, we found that a dense (with a density close to the theoretical, 3.02 g/cm^3), pure (with no specially added impurities) beryllium ceramic with a defined predominant orientation of the microcrystals in it can be material suitable for use as an ultrasound conductor in the 100 – 300 K temperature range.

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